

Towards a point spread function for nanoscale chemical imaging

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Background – Atomic force microscopy-infrared (AFM-IR) is an AFM based technique that measures mid-IR absorption spectra at nanometre spatial resolution. One of the most attractive advantages of AFM-IR for chemical spectroscopist is that it provides spectra which compare well to conventional FTIR absorption spectra [1]. The technique of AFM-IR relies on the detection of the pulsed wavelength tuneable IR laser induced thermal expansion of the sample area underneath the AFM tip. While this mode of signal generation sounds simple enough it is still not fully understood.

In this work, we present a theoretical investigation of the laser heating induced thermal expansion process and model it as a point spread function (PSF). This approach draws parallels to super resolution microscopy where the PSF is used to determine spatial resolution and to resolve features below the diffraction limit. The biggest challenge in determining the PSF of AFM-IR is the fact that it relies on the thermal diffusion process and depends on material and sample properties in addition to laser repetition rates and pulse lengths. Nevertheless, we theorize, that the AFM-IR signal in many real-world samples can be approximated using Green's functions for semi-infinite, homogenous media.

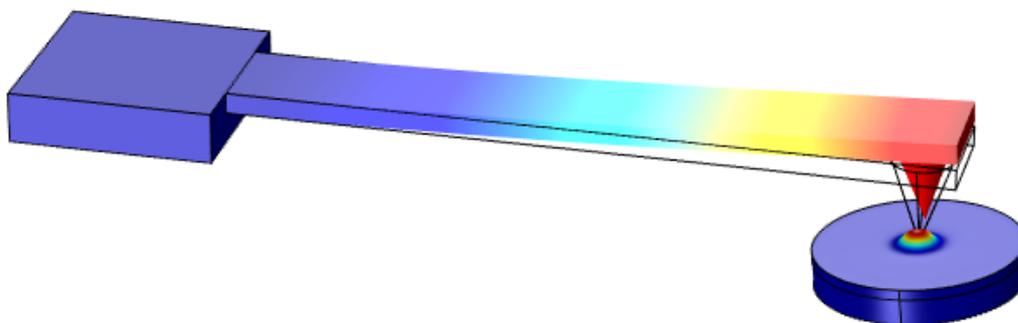


Fig. 1. Finite element simulation of thermal expansion of a spherical absorber by IR laser irradiation and detection by AFM cantilever in COMSOL.

Methods – In a homogeneous sample the resolution in an AFM-IR experiment is determined by how the temperature increases and distributes inside the sample following each laser pulse, hence it is governed by the Fourier's law [2]

$$\frac{1}{\alpha} \frac{\partial T}{\partial t} = \frac{Q}{V\kappa} + \Delta T \quad \text{Eqn. 1}$$

Where α is the thermal diffusivity, κ is the heat conductivity and V the volume size of the sample. $Q(t)$ is a volumetric heat source which linked to the laser heating. If the sample geometry is simplified enough (substrate replaced by heat sink, air layer replaced by insulating boundary, homogeneous and semi-infinite slab sample), Green's functions can be used to calculate the evolution of the sample after each laser pulse. These same Green's functions, evaluated at specific laser

pulse repetition rates then serve as AFM-IR's PSF. To verify that these simplifications do not result in a significantly changed behaviour a finite element model of heat conduction in solids and fluids (implemented in COMSOL Multiphysics 5.6) of more realistic sample geometries is used. In this case we consider a cylindrically shaped sample with a single spherical element thermally heated by a laser pulse. The sample is placed on a thick substrate and covered by an air layer (see fig. 2).

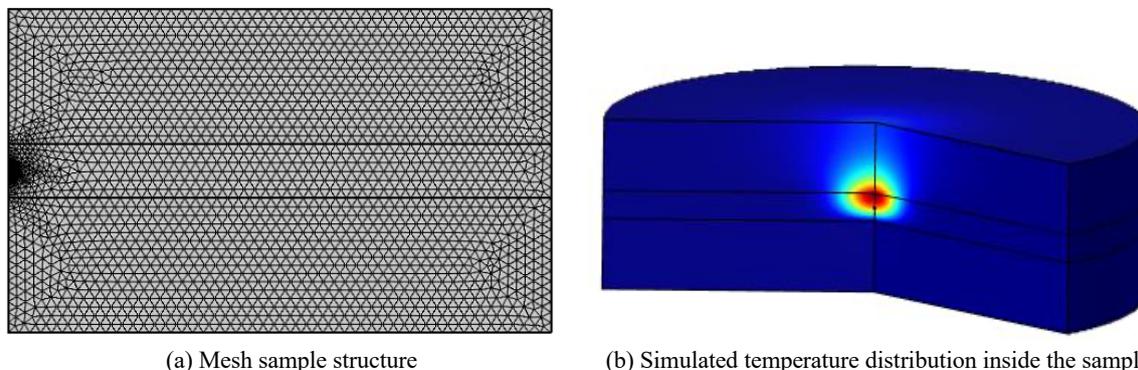


Fig. 2. Designed sample structure and heat transfer in solid and fluid model with COMSOL Multiphysics. The top layer is air, bottom layer is substrate and middle layer is sample matrix with buried single molecule in the middle.

Finally, the theoretical considerations yielding the PSF are compared to experimental data. Test samples are prepared by embedding fluorescent labelled spherical absorbers in a polymer matrix. Confocal fluorescence microscopy is used to determine the lateral and vertical information of the buried molecules and localize the positions where molecules might be among the centimetre scaled sample absorbers. Then the same sample area is measured in AFM-IR.

Results and Conclusion – First results show that there is a frequency (pulse repetition rate), pulse length and sample geometry dependence of the PSF in AFM-IR. The achievable spatial resolution is improved for short pulses, high frequencies and when the absorbers are closer to the substrate. These results provide guidance for experimental parameters which can be considered as trade-off between spatial resolution and signal intensity.

References

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- [2] D.W. Hahn, M.N. Özışık, Heat conduction, John Wiley & Sons, 3rd ed. (2012).